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WING OF THE RAYLEIGH LINE RECORDED WITH A SELF-RECORDING GRATING SPECTROPHOTOMETER

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(*Received March* 29, 1961)

ABSTRACT. A self-recording spectrophotometer has been constructed using a Bausch and Lomb plane grating with Ebert mounting, a thirteen-dynode photomultiplier, a D.C. amplifier and a Honeywell-Brown pen recorder. The resolution is found to be much higher than that given by the commercial recording spectrophotometers in which prisms are used as the dispersing system.

The wing of the Rayleigh line due to benzene at different temperatures and that due to liquid oxygen have been studied with this instrument. Benzene at 5°C shows two broad maxima in the wing which disappear when the liquid is heated to 75°C. Liquid oxygen shows a feeble wing with inflections about 38, 49 and 60 cm^{-1} away from the Rayleigh line. These results have been discussed.

INTRODUCTION

The use of plane grating with Ebert mounting (Ebert, 1889) as the dispersing system in a recording monochromator was discussed recently by Fastie (1952) who constructed such a monochromator with a resolving power of about 91000 in the first order. Besides the high resolving power the monochromator has also high light gathering power. In this respect such a monochromator is better than most of the commercial recording spectrophotometers in which prisms are used as the dispersing system. A recording spectrophotometer with high resolving power has another advantage which is not possessed by spectrographs having high resolving power. For studying the relative intensity of a weak satellite or a feeble wing close to an intense line the photographic method is quite unsuitable, because the exposure necessary to record the weak satellite makes the stronger line overexposed and scattering in the grains of the emulsion makes the width of the line much larger than its actual width produced by the dispersing system. Therefore, the photographic method is unsuitable for the study of distribution of intensity in the wing of the Rayleigh line. As the true distribution of intensity in the wing might throw some light on the structure of the liquid a programme was undertaken to study it with the help of a self-recording grating spectrophotometer and an attempt was made to construct a spectrophotometer similar to the monochromator constructed by Fastie (1952). The performance of such a spectrophotometer constructed in the laboratory and also some preliminary

results of investigations on the distribution of intensity in the wing of the Rayleigh line have been discussed in the present paper.

DESCRIPTION OF THE SPECTROPHOTOMETER

A Bausch and Lomb plane grating of dimensions 65 mm × 76 mm with 2160 grooves per mm and blaze angle of 40°23′ was used as the dispersing system. A schlieren mirror having a radius of curvature 150 cm and aperture about 20 cm was used both for collimating the incident beam and focusing the diffracted beam on the exit slit. The mounting is symmetrical, the plane of the grating is vertical and the scanning arrangement is similar to that in Fastie's monochromator. The reversible D.C. motor used for the scanning is, however, run by a stabilised voltage.

A 6256 photomultiplier tube supplied by E.M.I. Research Laboratories of England is used as the detector. The tube is mounted coaxially in a horizontal brass cylinder surrounded by a spiral of copper tubing through which alcohol cooled by liquid oxygen can be circulated to cool the photomultiplier tube. The window of the brass cylinder is provided with an annular electric heater to prevent condensation of moisture on the window of the photomultiplier tube. The maximum voltage applied to each dynode is about 155 V. A voltage stabliser purchased from Hungary and capable of supplying 3000 volts is used to supply the voltages to the dynodes. The electron current from the anode can flow

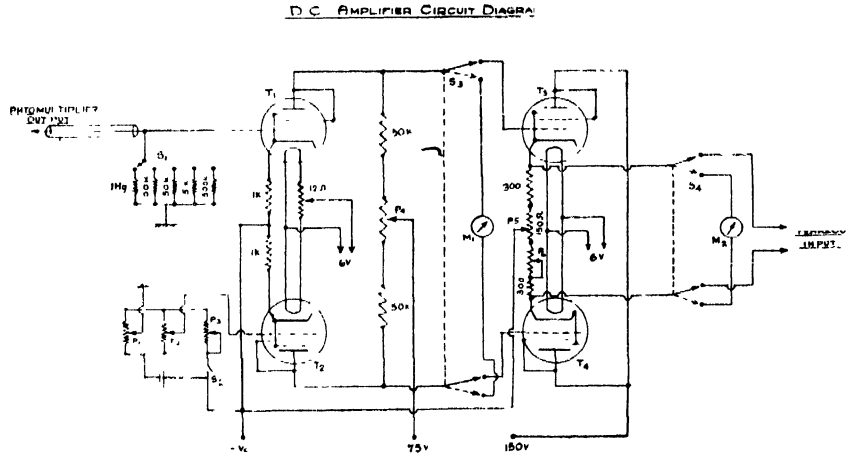


Fig. 1. Circuit diagram of D.C. amplifier.

through any one of the resistances of values 10K, 40K, 100K and 1 Megohm depending on the sensitivity required.

The output voltage of the photomultiplier tube is amplified by a D.C. amplifier designed on the principles of the circuit used by Chien and Bender (1947). The circuit had, however, to be modified in order to make it suitable for use with a Honeywell and Brown pen recorder. It was found initially that when the potential-drop across a high resistance was used to drive the pen recorder the pen became sluggish during its return sweep, broadening thereby the base of the peak due to any spectral line. So, the output of the balanced-bridge D.C. amplifier was fed to two cathode followers in balanced condition to reduce the effective resistance. The circuit diagram is given in Fig. 1. A photograph of the whole assembly is reproduced in Fig. 2.

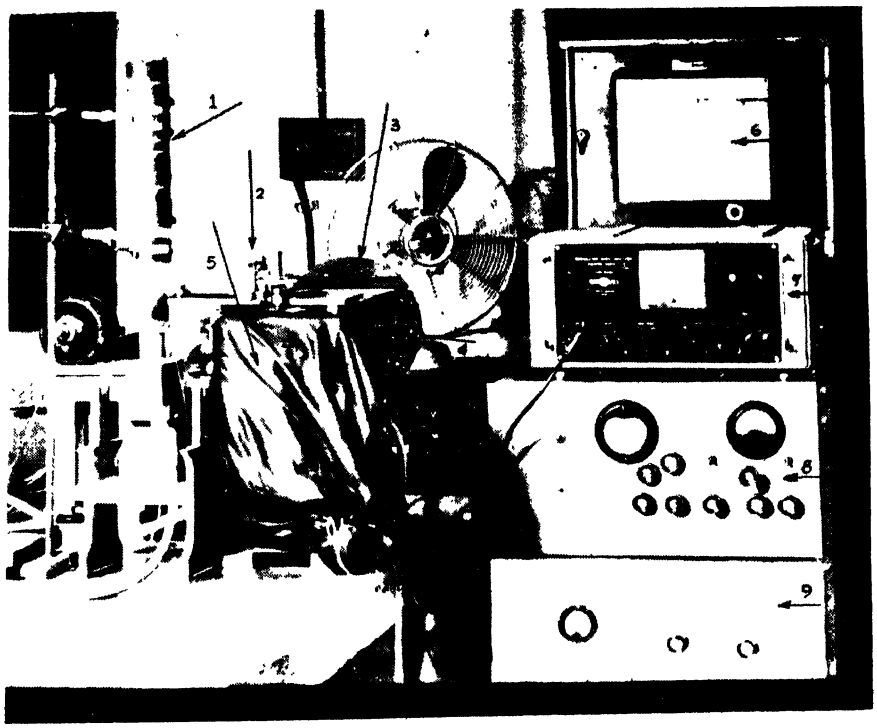


Fig. 2. Photograph of the recording spectrophotometer 1—Unsilvered Dewar flask of Pyrex glass, 2—Gear system for turning the grating, 3—Schuhcren concave mirror, 4—All-metal body of the spectrograph, 5—Photomultipher mount covered with black cloth, 6—Pen recorder, 7—High voltage stabilizer, 8—D. C. amplifier, 9—Stabilizer for D. C. amplifier.

EXPERIMENTAL

In order to study the wing of the Rayleigh line due to benzene a horizontal Raman tube of diameter about 25 mm provided with a jacket was used. Ice-cold water was first circulated through the jacket and the temperature of the

liquid was thereby brought down to 5°C. After recording the wing accompanying the Rayleigh line 4047A of Hg, the liquid was heated to 75°C by circulating hot water through the jacket and the wing in the same region was again recorded. Several records were taken for each of the temperatures to verify the genuineness of the curves.

A special Dewar vessel of Pyrex glass was made for studying the wing due to liquid oxygen. Two plane parallel Pyrex discs were fused parallel to each other in a horizontal position in the two walls at the bottom of the Dewar vessel. A Pyrex glass tube with blackened tail and closed at the lower end was placed inside the Dewar vessel with its tapered and blackened tail at the top. The Dewar vessel was then filled up with liquid oxygen filtered with filter paper. The liquid filled the inner tube by entering into it through a hole in its wall. The scattered light coming out through the bottom of the Dewar vessel was reflected by a right-angled prism and focussed with a long-focus lens on the entrance slit of the spectrophotometer. Finally, the record of the spectrum of the mercury lines reflected by gray paper was taken to compare the width of the peaks with those due to the scattered light.

RESULTS AND DISCUSSION

The records of the Raman spectra due to CCl_4 and $CHCl_3$ are reproduced in Figs. 3(a) and 3(b). The spectra of light scattered by benzene at 5°C and 75°C are reproduced in Figs. 4 and 5 respectively and Fig. 6 shows the spectrum due to liquid oxygen. The record of the spectrum of incident light is also reproduced in Fig. 7 for comparison.

It is evident from Fig. 4 that the wing due to benzene at 5°C shows two broad maxima at about 44 cm^{-1} and 73 cm^{-1} respectively with a continuous background between them and the curve due to benzene at 75°C given in Fig. 4 shows that there is only one inflexion at about 49 cm^{-1} and that the curve extends upto a shorter distance. Crystals of benzene at −10°C show three lines at 44, 60 and 100 cm^{-1} respectively (Sirkar and Ray, 1950) and the frequency-shifts increase to 48, 60 and 116 cm^{-1} respectively when the temperature of the crystals is lowered to − 100°C. The broad maxima at 44 cm^{-1} and 73 cm^{-1} in the wing due to the benzene at 5°C may therefore correspond respectively to the lines 60 and 100 cm^{-1} due to the crystals at − 10°C, the frequency-shifts diminishing with the rise of temperature from − 10°C to 5°C and with the change of state. The band corresponding to the line 48 cm^{-1} of the crystal may have merged with the strong half-width of the Rayleigh line which extends up to about 38 cm^{-1} from the centre of the line in this case. All these facts show that these bands are not produced by the rotation of the molecules in the liquid state but they originate most probably from vibrations in groups of molecules which are formed in the liquid at 5°C and break up when the temperature is raised to 75°C. The

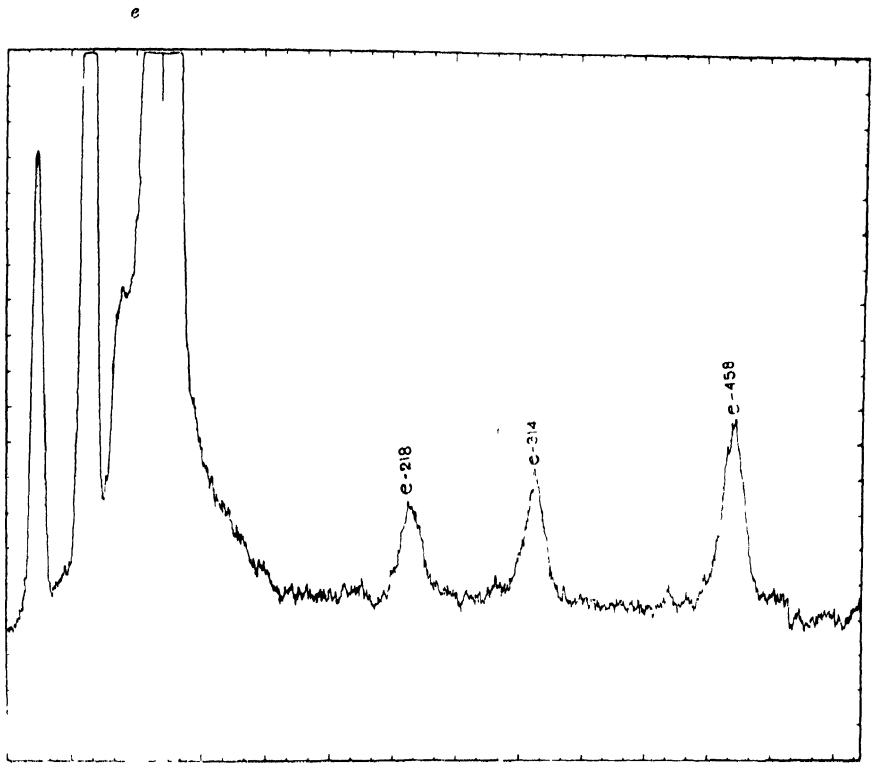


Fig. 3(a). Raman spectrum of CCl_4.

sharp lines observed in spectra of the crystals are therefore produced by such vibrations in groups of molecules, the intermolecular bond being slightly stronger in the case of the crystals. These results confirm the observations made by Kastha (1958) who studied the distribution of intensity in the wing of the Rayleigh line due to a few organic liquids at different temperatures and found evidence of formation of groups of molecules giving rise to continuous wing at temperatures a few degrees above the melting points of the substances.

A comparison of the curve due to the 4046 A line of Hg scattered by liquid oxygen reproduced in Fig. 6 with that due to the incident line shown in Fig. 7 indicates that the scattered line is much broader than the incident line probably due to the existence of a strong wing close to the Rayleigh line. The peak is unsymmetrical due to sulggishness if the pen during return sweep. It is further observed that on the Stokes sides of the 4046 A line the wing extends upto about 100 cm^{-1} from the centre of the Rayleigh line and there are inflexions at distances of about 38 cm^{-1}, 49 cm^{-1} and 60 cm^{-1}, the intensity falling off rapidly after each inflexion. It would be interesting to compare these results with those due to the gas. Unfortunately, the spectrum due to the gas at a temperature just above $-180°C$ has not been investigated by any

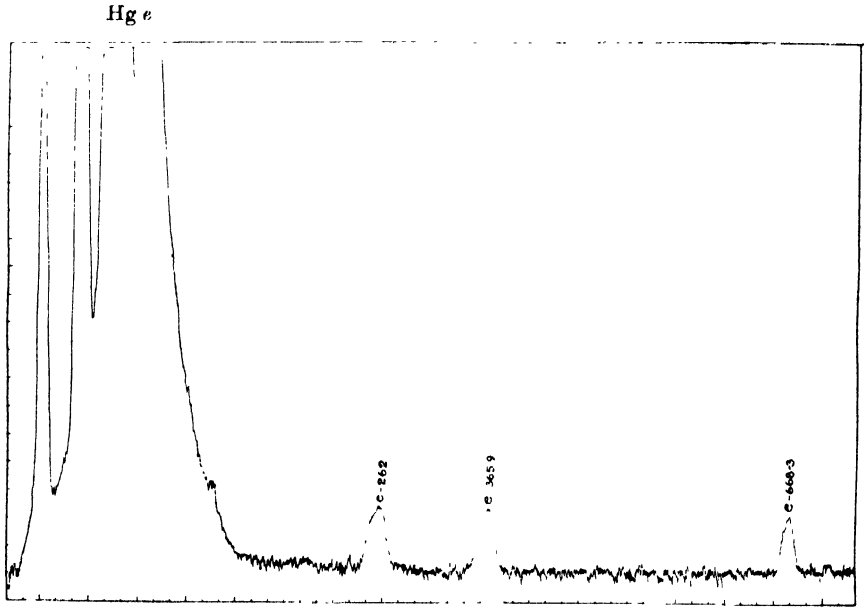


Fig. 3(b). Raman spectrum of $CHCl_3$.

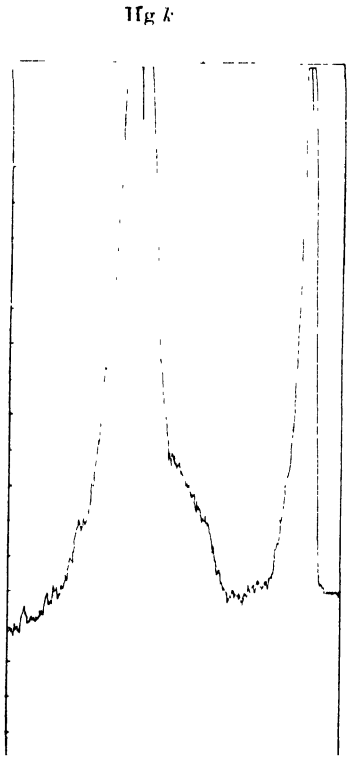


Fig. 4. 'Wing' due to benzene at 5°C.

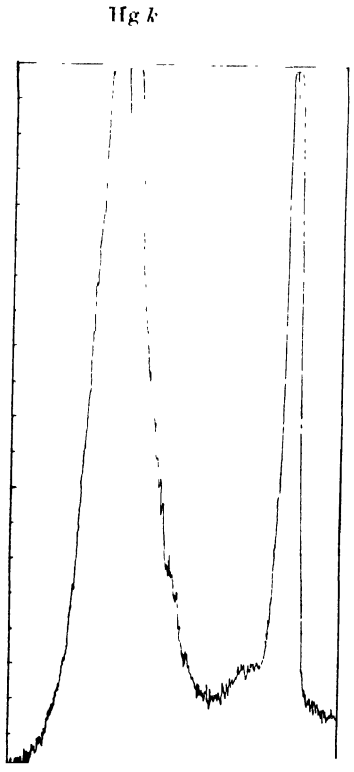


Fig. 5. 'Wing' due to benzene at 75°C.

previous worker. Theoretical values of the relative intensities of the rotational lines of O_2 at $-120°C$ are given in Table I.

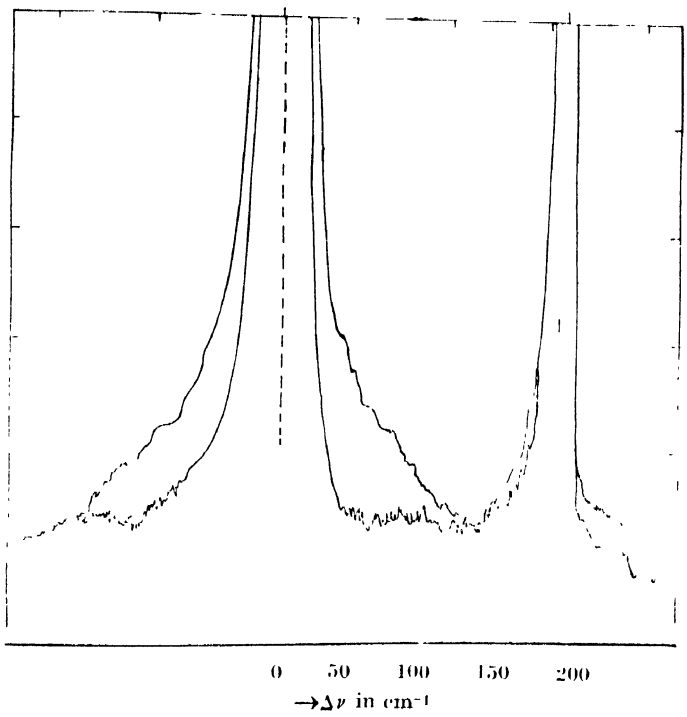


Fig. 6. Rotational wing due to liquid oxygen.

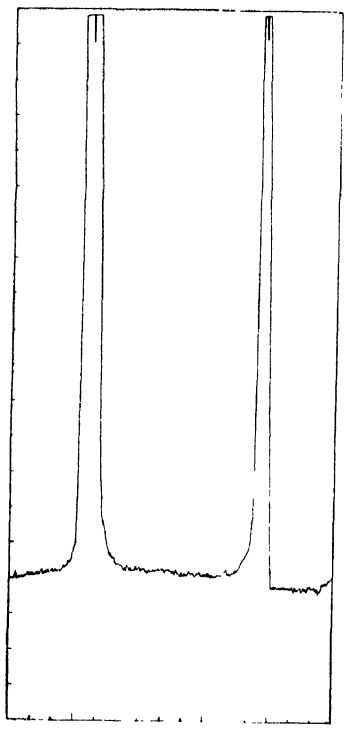
TABLE I

Initial value of J	$\Delta\nu$ in cm^{-1}	Relative intensity in arbitrary units
1	14.26	0.153
3	25.88	0.226
5	37.36	0.221
7	48.88	0.160
9	60.20	0.092
11	71.80	0.042

It can be seen from Table I that the second and third rotational Raman lines of O_2 are expected to be almost of the same intensity and the strongest lines in the rotational spectrum. The fourth line at about 49 cm^{-1} would be much weaker than either of these two lines and the fifth line should be less than half as intense as the second or the third line. The inflexions at 38 cm^{-1},

49 cm^{-1} and 60 cm^{-1} observed in the spectrum of liquid oxygen at −180°C agree closely with the rotational lines of O_2 at 180°C both in respect of positions and relative intensities. The appearance of broad inflexions in place of sharp peaks shows that the intermolecular collision in the liquid broadens the lines.

The region from the edge of the Rayleigh line upto about 14 cm^{-1} would be free from any scattered intensity theoretically, but Fig. 6 shows an intense scattering in this region extending upto about 35 cm^{-1} and masking the two rotational maxima at about 14.26 cm^{-1} and 25.88 cm^{-1}. This broadening is not due to any difference in the intensities of the Rayleigh line and the inner incident line reproduced in Fig. 6, because the width of the line 4077 A is the same in both the cases. It has to be concluded, therefore, that probably some of the O_2 molecules form O_4 molecules with loose coupling between them so that the vibration and rotation of such dimeric molecules produce a strong wing extending upto about 35 cm^{-1} from the centre of the Rayleigh line.



Fig, 7. Record of incident Hg lines.

The wing of the Rayleigh line due to liquid oxygen was studied previously by several workers by using prism spectrographs and photographic method. Saha (1940) first observed a continuous wing with a maximum at a distance of 50 cm^{-1} from the centre of the Rayleigh line. Later, Crawford *et al.* (1952) reported that they failed to detect any maximum in the continuous wing due to

liquid oxygen. Kastha repeated the investigation in 1954 and by carefully superposing the microphotometric record of the incident mercury line 4047 Å on that of the line scattered by liquid oxygen, found a maximum at 40 cm^{-1} from the Rayleigh line in the continuous wing due to liquid oxygen. The distances of the maximum found by Kastha (1954) is almost the same as that of the first inflexion observed in the present investigation, but the larger intensity upto 35 cm^{-1} from the edge of the Rayleigh line could not be detected by Kastha (1954) The photographic method is thus inferior to the photoelectric method for such an investigation when in the latter case a grating with high resolving power is used, so that the wing is clearly separated brom the Rayleigh line.

ACKNOWLEDGMENT

The authors' thanks are due to Dr. A. R. Deb who rendered some help in the intital stages of the construction of the spectrophotometer and to the staff of the workshop of the Association who made some parts of the spectrophotometer and assembled the different parts to make the complete instrument.

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